NASA-CR-203942

Sol-gel Coatings for Enhancing Ceramic and Metallic Thermal Protection Systems

NAS2-14063

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Report Prepared for
NASA Ames Research Center
MS 223-4
Moffett, CA 94035

December 1994

I. Introduction

Ceramic and metallic Thermal Protecting Systems (TPS) are both being considered for use on planned SSTO. Ceramic TPS are porous and provide significant insulation at low pressures. The primary type of ceramic insulation currently in use is Reusable Surface Insulation (RSI). Nearly 25,000 RSI tiles are used on the Space Shuttle Orbiter. The materials used in ceramic TPS are easily wetted by water, due to a high concentration of vicinal hydroxyl groups. These groups undergo hydrogen bonding, which promotes the absorption of water. Fibrous ceramic TPS could easily become saturated with dew or rain water while being prepared for launch. Currently, dimethylethoxysilane (DMES) is used to waterproof ceramic TPS. However, this organic waterproofing agent is not stable at re-entry temperatures and must be reapplied after each mission. This results in extra expense and impedes a rapid return to orbit. Sol-gel coatings may act as a permanent waterproofing agent by forming a lasting inorganic surface layer that does not form vicinal hydroxyl groups.

A leading metallic TPS for SSTO applications is a superalloy honeycomb sandwich, in which fibrous insulation is sandwiched between an Inconel 617 honeycomb external panel and a titanium honeycomb internal panel. The metallic TPS require enhanced emittance, reduced catalytic activity, and high oxidation resistance. The IN 617 has very high catalysis, good oxidation, and good emittance characteristics after the initial exposure to high temperatures.

In this work, we studied the effect of various thin oxide coatings on the surface properties of both ceramic and metallic TPS. The oxide coatings were applied by a sol-gel process. Ceramic insulation was coated with a permanent, nonvolatile waterproofing agent. In the case of metallic TPS, improved emittances, reduced catalytic efficiencies, and high oxidation resistances were achieved by applying sol-gel coatings.

II. Experimental

Various experimental techniques have been used to study the beneficial effects of ceramic coatings on ceramic and metallic TPS. Some of the techniques used in this study are briefly discussed below.

Contact Angle Measurements

The relationship between surface and interfacial energies determines the wetting behavior of a liquid on a solid surface. The angle between the solid surface and the tangent to the liquid surface at the contact point is defined as the contact angle. Liquids with wetting angles of 90° or less are considered to wet the solids, while those with angles greater than 90° do not wet. Contact angles can be computed using the following formula:

$$\tan(\theta/2) = 2h/d$$

where h is the height of the drop, d is the diameter of the drop, and θ is the contact angle. Both h and d values are measured using a traveling microscope.

Fourier Transform Infra Red (FTIR) Spectroscopy

FTIR spectroscopy was used to identify and measure the concentration of vicinal hydroxyls on a solid surface. The concentration of vicinal hydroxyls indicates the overall tendency for the solid surface to promote wetting by aqueous media. By observing the strengths of the absorption bands, the presence of isolated hydroxyls, vicinal hydroxyls, and absorbed water can be compared.

Emittance Measurements

Emittance was measured using a government-furnished heated-cavity reflectometer. Reflection measurements as a function of wavelength were used to calculate the total emittance of a surface at ~982°C. This was accomplished using Kirkoffs rule and integrating the spectral emittance against the blackbody radiation curve for a given temperature.

Catalysis Measurements

Catalysis measurements were done using an arc jet wind tunnel with sufficiently high enthalpies to simulate the dissociated airflows encountered in hypersonic flight. Two measurements were performed in a government furnished arc-jet facility: 1) cold-wall heating rate, from which cold-wall catalytic efficiency was calculated: 2) steady-state heat flux, from which hot-wall catalytic efficiency was calculated. Most surfaces become more catalytic as the temperature is increased. Therefore, it is very important to establish steady state conditions for measuring hot-wall catalytic efficiencies. Cold-wall catalytic efficiencies are not representative of the conditions of interest, but hot-wall measurements, while more difficult to make, are of much greater value.

III. Results and Discussions

Coatings for Waterproofing Ceramic Fibrous Insulation

Initially, nonvolatile and water insoluble high-temperature oxides such as Nb_2O_5, Ta_2O_5, TiO_2, ZrO_2, $ZrSiO_2$, $CeZrO_2$, and $CaZrO_3$ were identified for investigation. These oxide coatings were applied on glass slides using the sol-gel process to study the wettability of the coatings.

Wettability of Coatings

The contact angles measured on various ceramic compound surfaces are shown in Table I. It is evident from the table that the contact angles on the ZrO_2 or modified ZrO_2 coated surfaces are the largest among the water insoluble oxides. The effect of partial substitution (up to 5%) of cations such as Ce, Ca, Mg, Si, Ti, and Y for Zr in ZrO_2 on the contact angles was studied. In general, a slight improvement in the contact angles was observed by increasing the curing temperature from 600°C to 1000°C. The additions of Si, Ti, and Y to ZrO_2 improved the wettability (decreased the contact angles) of ZrO_2, whereas the Ce and Mg additions did not significantly affect the contact angles. On the other hand, Ca substitution in ZrO_2 resulted in slightly higher contact angles which are greater than 90°.

Photographs showing the shapes of de-ionized water droplets of the same weight on a 5%$CaZrO_2$ coated and an uncoated surface are shown in Figs. 1 and 2, respectively. The contact angle for the coated surface, measured from the photograph from the values of height of the drop and diameter of the drop, is in the 90° - 93° range, indicating the non-wetting nature of 5%$CaZrO_2$ surfaces.

Wettability of the oxide surfaces were also examined using the capillary tube method. This method involves the measurement of the capillary rise in the tube after insertion into a container of de-ionized water. The capillary rise is proportional to the wettability of the surfaces. The capillary tubes were sol-gel coated and cured at 600°C. The capillary height for the uncoated and ZrO_2 coated tubes are approximately15 mm and 4 mm, respectively. This observation again indicates the non-wetting nature of ZrO_2 surfaces. In this method, the capillary tube materials limited the maximum curing temperature to 600°C.

FTIR Spectroscopy

Cabosil is a high surface area silica powder which is chemically similar to crystalline quartz and fibrous silica. Figures 3 and 4 show the Fourier Transform Infra Red (FTIR) spectra of the uncoated cabosil and ZrO_2 coated cabosil, respectively, after curing at 550°C for 1 hr. These spectra were obtained after cooling the cabosil samples to room temperature on the same day the coating was applied. Peaks labeled 1, 2, and 3 correspond to isolated surface hydroxyls, vicinal hydroxyl groups, and pure cabosil, respectively. The strength of individual absorption peaks is proportional to the concentration of respective chemical bonds. On comparison of the strengths of peaks in these two spectra, it is evident that the cabosil coated with ZrO_2 has a higher concentration of vicinal hydroxyl groups (peak 2) compared to the uncoated cabosil. It is well known that ceramics with higher melting temperatures will take a longer time to attain surface equilibrium than the ceramics with low melting temperature. Since the higher concentration of vicinal hydroxyls in the ZrO_2 coated cabosil is probably due to non-equilibrium conditions, the samples were left in air for few days and the FTIR measurements were taken again. Figure 5 shows the FTIR spectra from the same uncoated and ZrO_2 coated samples, respectively, after leaving in air for a few days. The diminished vicinal hydroxyl group peak in Fig. 5 indicates a lesser concentration of vicinal hydroxyls in the ZrO_2 coated cabosil, which is an important criteria in the selection of a permanent waterproofing agent. The concentration of vicinal hydroxyls in the ZrO_2 coated cabosil was further reduced by heat treating at 1000°C for 1 hr. The FTIR spectrum obtained after curing at 1000°C is shown in Fig. 6.

Immersion Testing

ZrO_2 and 5%$CaZrO_2$ were identified as possible agents for permanent waterproofing for ceramic TPS. Ta_2O_5 coatings were also tested along with ZrO_2 and 5%$CaZrO_2$ for comparison. Immersion testing was carried out on the coated and uncoated micro quartz batting material (100% SiO_2), Q-felt insulation, and Composite Flexible Blanket Insulation (CFBI). Fibrous micro quartz material was coated with ZrO_2, 5%$CaZrO_3$, and Ta_2O_5 sols of different concentrations. The samples were then cured at 1000°C for 1 hr and were left in air for a day in order to attain equilibrium conditions. The weights of the samples were obtained after the curing process. The coated and uncoated samples were immersed in water for 30 minutes and the weights were again obtained. The volume of imbibed water is determined from weight gain measurements. Results of the immersion test are presented in Tables II, III, and IV for micro quartz fibrous insulation, Q-felt insulation, and Composite Flexible Blanket Insulation, respectively. These results indicate that the amount of imbibed water is lower in the ZrO_2 / 5%ZrO_2 coated insulation (for a given wt. % of coating material) than in the Ta_2O_5 coated and the uncoated insulation.

Table I. Results of Contact Angle Measurements.

Ceramic Compound	Curing Temperature (°C) and Time (min.)	Range of Contact Angles (in Deg.)
SiO_2 (uncoated glass slide)	none	32 - 37
SiO_2 (uncoated glass slide)	600 5	22 - 26
Ta_2O_5	600 5	37 - 41
Ta_2O_5	1000 60	54 - 57
Nb_2O_5	600 5	33 - 36
TiO_2	600 5	73 - 78
ZrO_2	600 5	84 - 87
ZrO_2	**1000** **60**	**87 - 92**
5%$CaZrO_3$	600 5	86 - 90
5%$CaZrO_3$	**1000** **60**	**91 - 94**
5%$MgZrO_3$	600 5	85 - 88
5%$SiZrO_2$	600 5	55 - 57
$SiZrO_2$	600 5	38 - 42
5%$CeZrO_2$	600 5	83 - 88

Figure 1. Photograph of water drop on a 5%$CaZrO_3$ coated surface (cured at 1000°C for one hour).

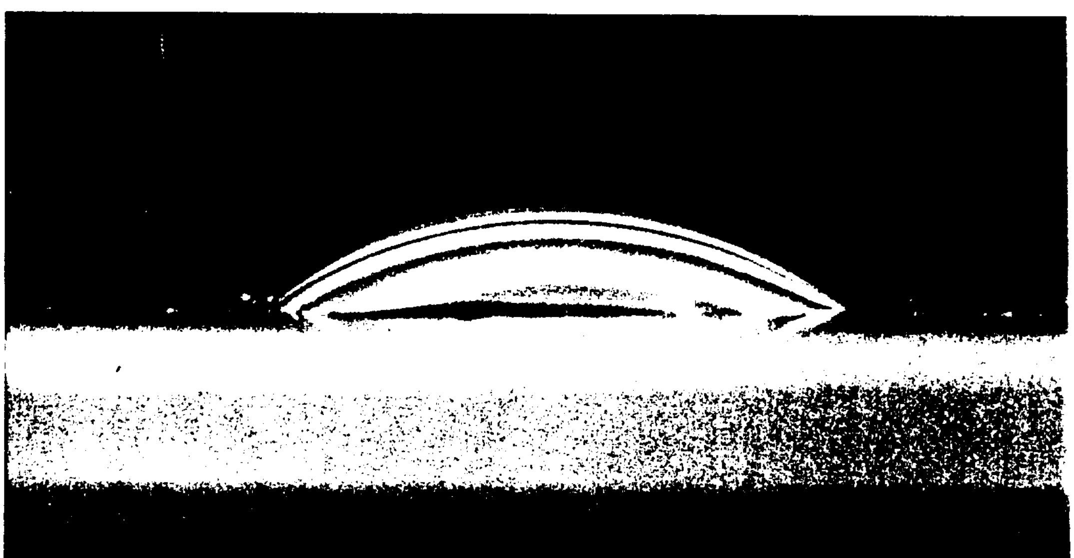

Figure 2. Photograph of water drop on an uncoated fused silica slide (cured at 1000°C for one hour).

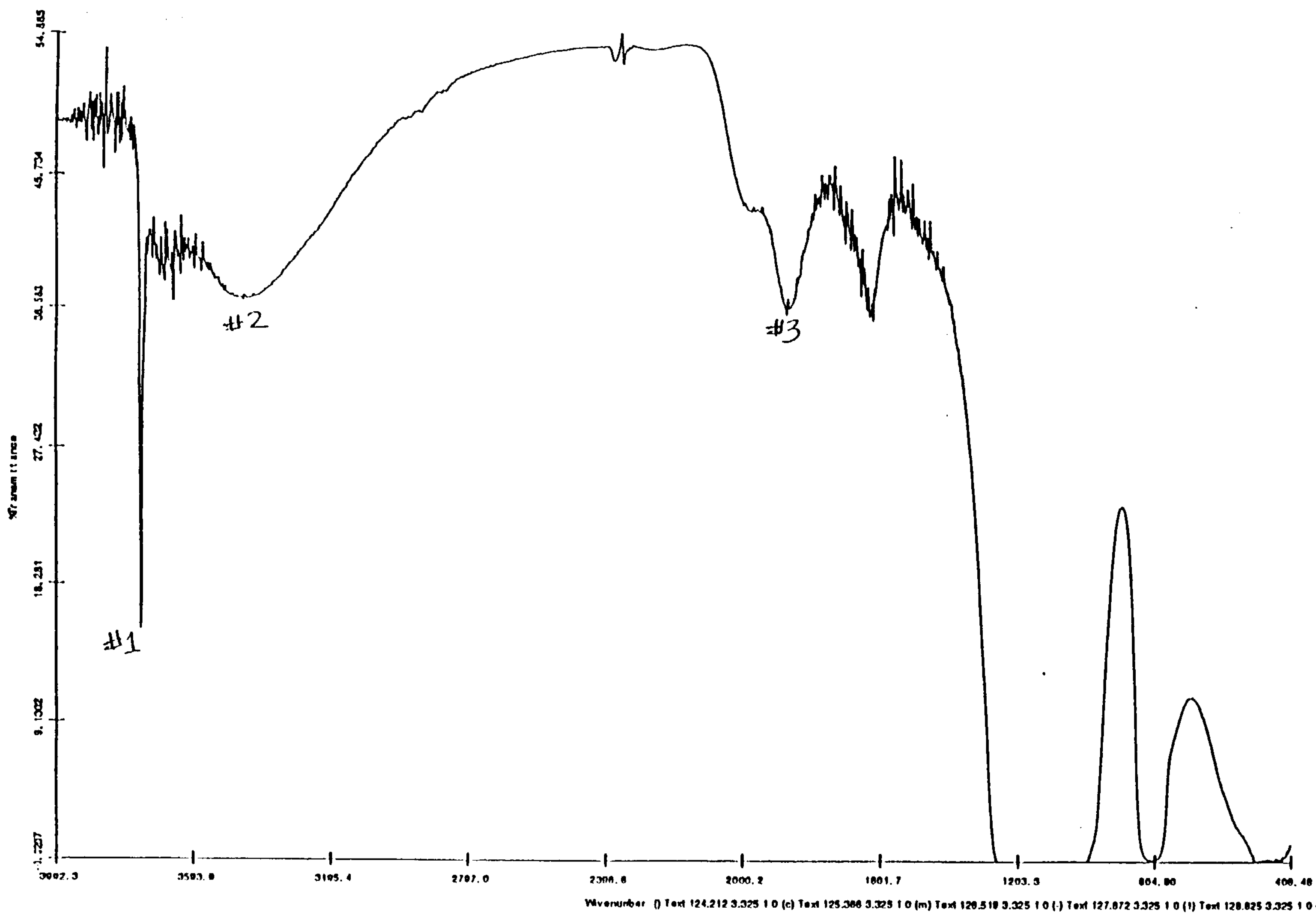

Figure 3. Infrared spectrum of uncoated cabosil powder after curing at 550°C for 1 hour.

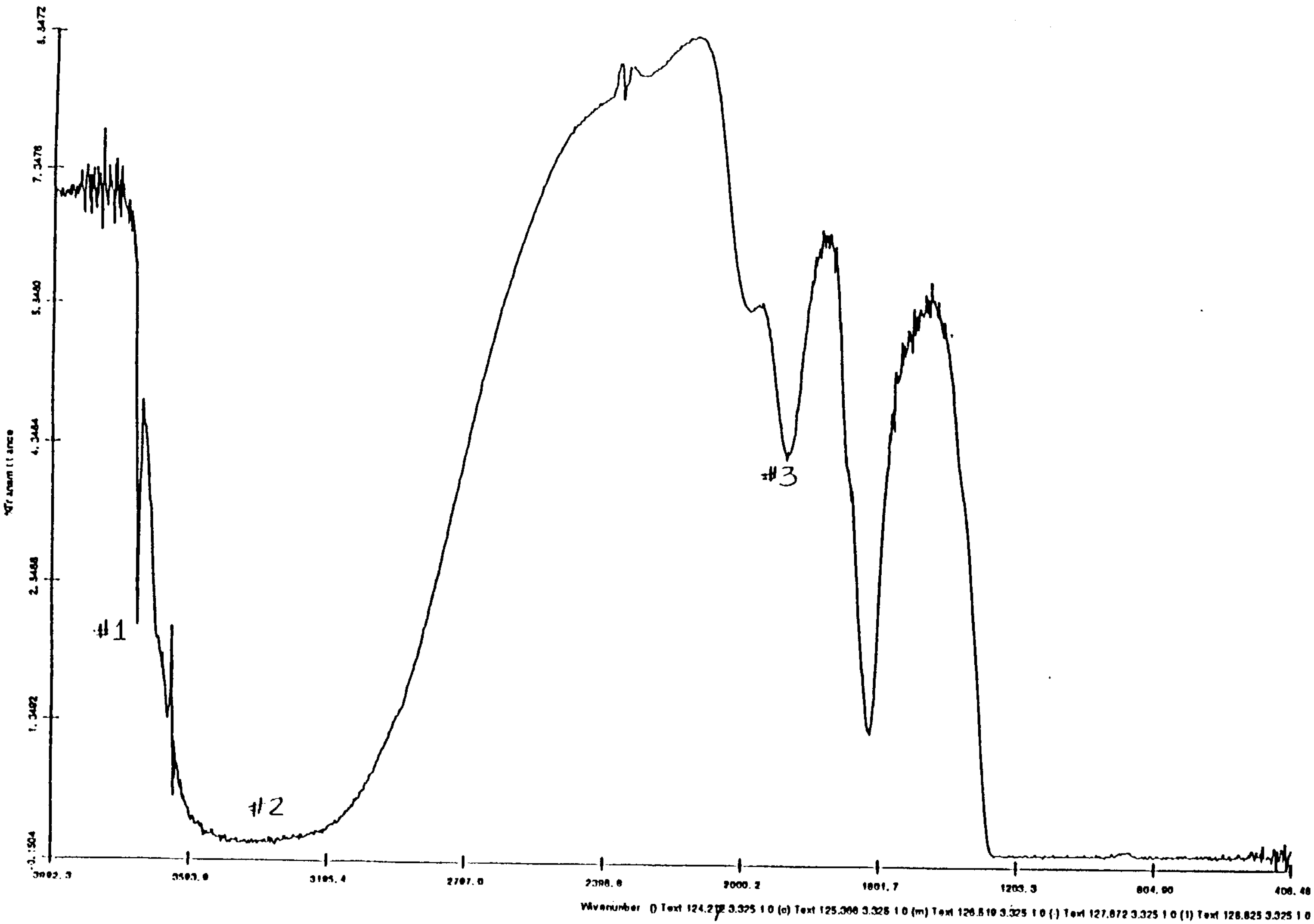

Figure 4. Infrared spectrum of ZrO_2 coated cabosil powder after curing at 550°C for 1 hour.

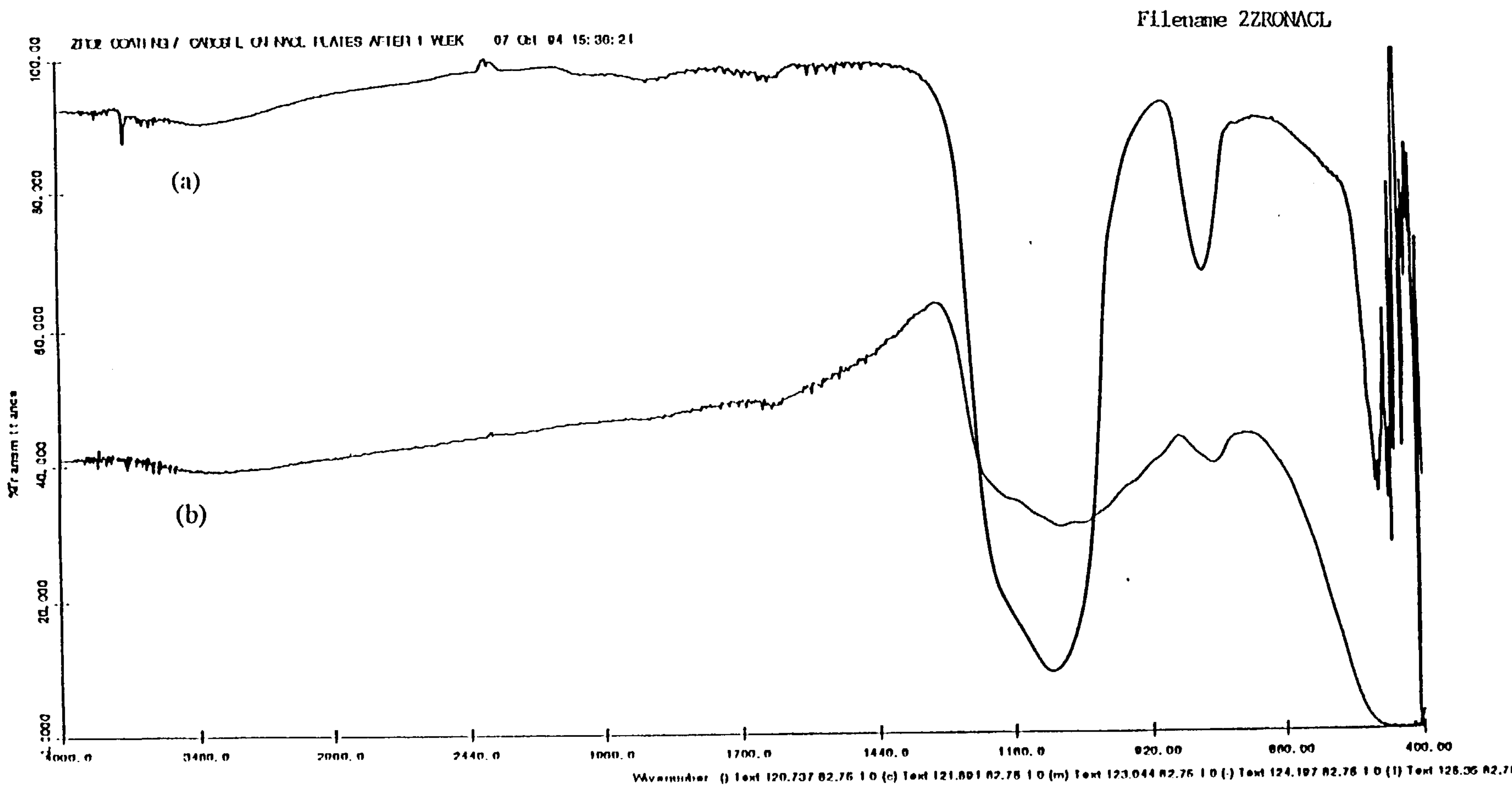

Figure 5. Infrared spectra of (a) uncoated and (b) ZrO_2 coated cabosil powder.

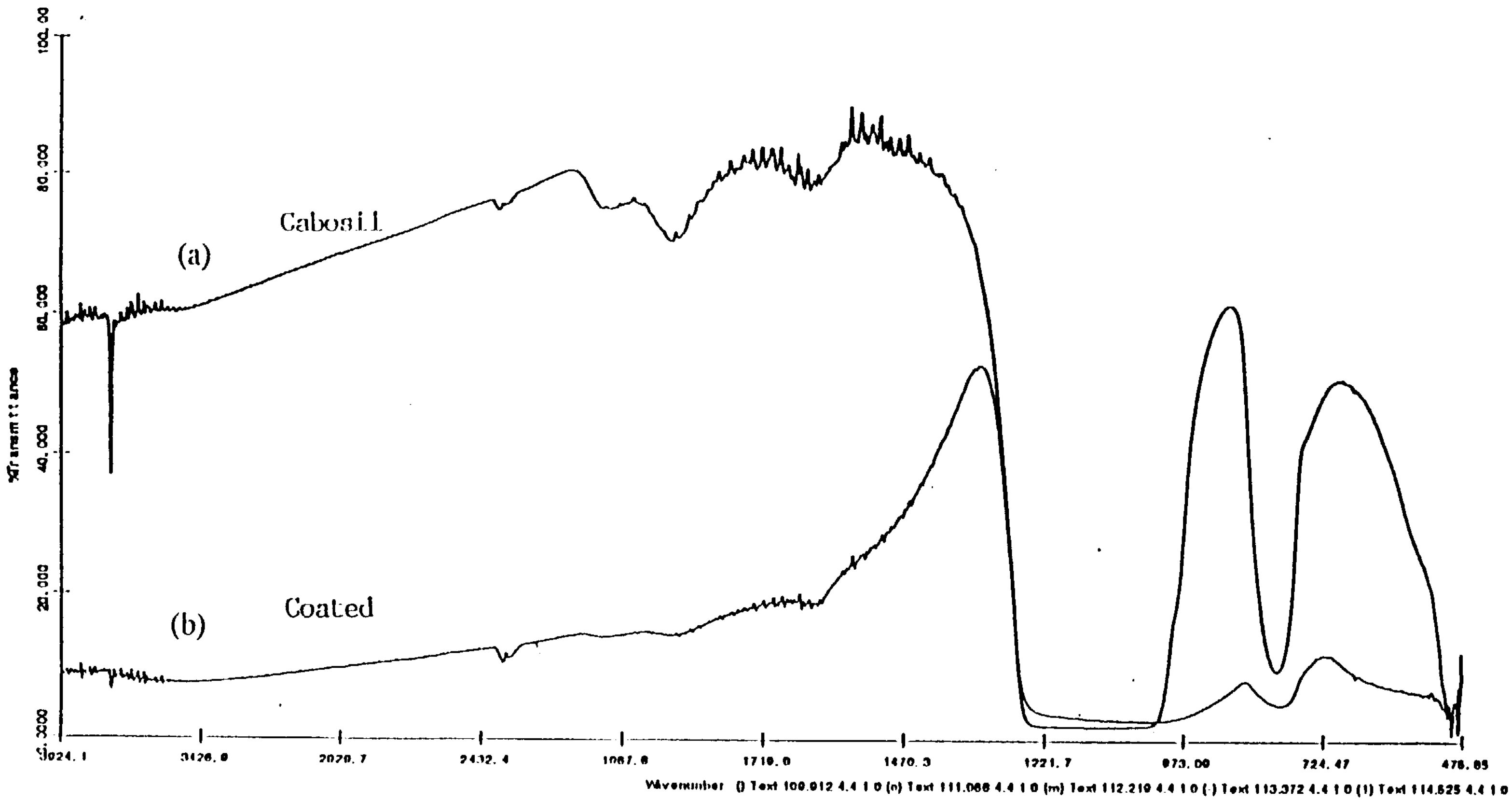

Figure 6. Infrared spectra of (a) uncoated and (a) ZrO_2 treated cabosil powder after curing at 1000°C for 1 hour.

Table II. Immersion test results for micro quartz batting material.

Coating Material	Wt. % of Coating	Weight (gm) Prior to Immersion	Weight (gm) After 30 min. Immersion	Weight Increase (%)
None	——	0.0354	0.4400	1142
Ta_2O_5	26.99	0.1620	1.1717	623
Ta_2O_5	3.93	0.0536	0.5717	966
ZrO_2	36.35	0.1912	1.0667	457
ZrO_2	11.84	0.0638	0.5547	769
ZrO_2	3.41	0.0420	0.3878	823
5%$CaZrO_2$	29.76	0.1519	0.9273	510
5%$CaZrO_2$	14.79	0.0541	0.3937	627
5%$CaZrO_2$	4.31	0.0551	0.5166	837

Table III. Immersion test results for Q-felt insulation.

Coating Material	Weight % of Coating	Weight (gm) Prior to Immersion	Weight (gm) After 15 min. Immersion	Weight Increase (%)
None	———	8.1242	170.4929	1999
ZrO_2	40.00	13.0804	89.7297	585
5%$CaZrO_3$	42.00	13.5626	85.1288	527

Table IV. Immersion test results for Composite Flexible Blanket Insulation (CFBI).

Coating Material	Weight % of Coating	Weight (gm)	Weight (gm)	Weight Increase (%)
		Prior to Immersion	After 15 min. Immersion	
None	_____	14.3058	61.1728	327
ZrO_2	20.00	18.2827	67.9960	271
5% $CaZrO_3$	19.35	17.8796	66.6290	272

Coatings for Thermal Control of Inconel 617

Metallic TPS materials need enhanced emittances, reduced catalytic activities, and high oxidation resistances. The effectiveness of various sol-gel coatings in protecting metallic TPS was evaluated. Several tests such as static and dynamic oxidaton, catalysis, and emittance were carried out on the coated and uncoated IN 617 samples.

Oxidation

Accelerated oxidation tests were carried out on Two-Phase Glass (TPG) coated, 80 at.% Si - 20 at.% Al alloy (Si-20 Al) coated, and uncoated Inconel 617 (IN617) discs to compare the various weight changes. The weight change curves for oxidation at 982°C and 1100°C are shown in Figs. 7 and 8, respectively. Similar weight gain data of the TPG and Si-20Al coated and uncoated IN 617 discs at 982°C indicates similarity in the oxidation behavior of the three samples. Similar data was obtained at 1000°C. At 1100°C, the weight change curve of the TPG coated sample falls off after approximately 40 hrs of exposure and is attributed to spalling of oxidized layers.

We also observed the evaporation of CrO_2/CrO_3 from the uncoated and Si - 20Al coated samples. In contrast, the CrO_2/CrO_3 evaporation was not observed in the TPG coated sample indicating that the TPG coating prevents Cr losses. However, the TPG coating starts to fall off after 40 hrs of exposure at 1100°C resulting in CrO_2/CrO_3 evaporation. All the above mentioned factors make it difficult to compare the weight change data at 1100°C.

The weight change of IN617 coated with the TPG coating in the HYpersonic Metallurgical Environmental Test Systems (HYMETS) facility exposed at ~982°C (1800°F) is shown in Fig. 9. It is evident from the figure that the weight change with the TPG coating is the smallest, which indicates that this coating is effective in extending life at this temperature.

Catalysis

Catalysis is a chemical property governing the recombination of dissociated oxygen and nitrogen. Recombination is a highly exothermic reaction, and at hypersonic velocities, the recombination is the greatest potential source of heat. Figures 10 and 11 show the recombination efficiency of uncoated and LaRC sol-gel coated IN617 as a function of HYMETS exposure time at 982°C (~1255 K). In each figure, both hot-wall and cold-wall recombination efficiencies are presented. The hot-wall measurements are representative of the conditions of interest because of the high temperatures involved. The recombination efficiencies of LaRC sol - gel coated IN 617 are lower than that for the uncoated IN617, particularly for exposures less than 1 hr. This indicates that the non catalytic coatings are effective on IN617.

Emittance

Figure 12 shows the spectral emittance of IN617 coated with the TPG coating as a function of wavelength after different HYMETS exposures. The spectral emittance increases with the HYMETS exposure and values as high as 0.85 were obtained in the desired wavelength range (0-10 micrometers). On the other hand, the spectral emittance in the as coated condition is low. Reflection measurements as a function of wavelength were used to calculate the total emittance of a surface at different temperatures. The results are shown in Table V. Note the increase in total emittance values after HYMETS exposure.

Figure 13 shows the spectral emittance of uncoated IN617 after bead blasting and static oxidation. It is evident from the figure that the spectral emittance increases with HYMETS exposure. Efforts to further increase spectral emittance values are in progress by sol-gel coating on the already treated (bead blasted and static oxidation) IN617 surfaces.

Concluding Remarks

The wettability of non-volatile and water insoluble ceramic oxides were examined to find permanent waterproofing agents for ceramic fibrous insulation. Of the several ceramic oxides examined, only ZrO_2 and $5\%CaZrO_2$ are non wettable. Immersion tests on the coated and uncoated micro quartz material indicates that the water absorption could be reduced by half by coating the micro quartz with ZrO_2 / $5\%CaZrO_2$.

Isothermal static oxidation of IN617 discs showed that both TPG and Si-20 Al coatings did not result in improved oxidation resistance of IN617. However, under hypersonic conditions, the TPG coating is effective on IN617 for oxidation resistance. Further, the ceramic coated samples yielded higher emittance values and lower catalytic efficiencies compared to the uncoated samples.

Suggested Future Work

Water adsorption characteristic of hydrophobic zeolites is very low (< 5%). Therefore, the potential use of hydrophobic zeolites for permanent waterproofing for ceramic fibrous insulation should be given a consideration. The suitability of Zr-modified TPG coating on IN617 for oxidation resistance needs to be studied. Efforts to further increase spectral emittance values are in progress by sol-gel coating on the already treated (bead blasted and static oxidation) IN617 surfaces.

Acknowledgments

This work was supported by NASA Ames Research Center, CA under contract NAS2-14063. The authors are grateful to Dr. R. K. Clark of LaRC for performing emittance, catalysis, and HYMETS measurements. The authors would also like to thank Mr. V. V. Raman for his useful discussions. The authors are also grateful to Teena Oliver, Anna Sample, and Greg Kostanski for their experimental assistance.

No. hrs.	uncoated	TPG coated	Si - 20Al coated		
0	0	0	0		
10	0.4218	0.3437	0.3124		
20	0.6092	0.5468	0.5312		
40	0.7499	0.7655	0.7342		
60	0.9061	0.9529	0.9217		
80	1.0311	1.1404	1.0779		

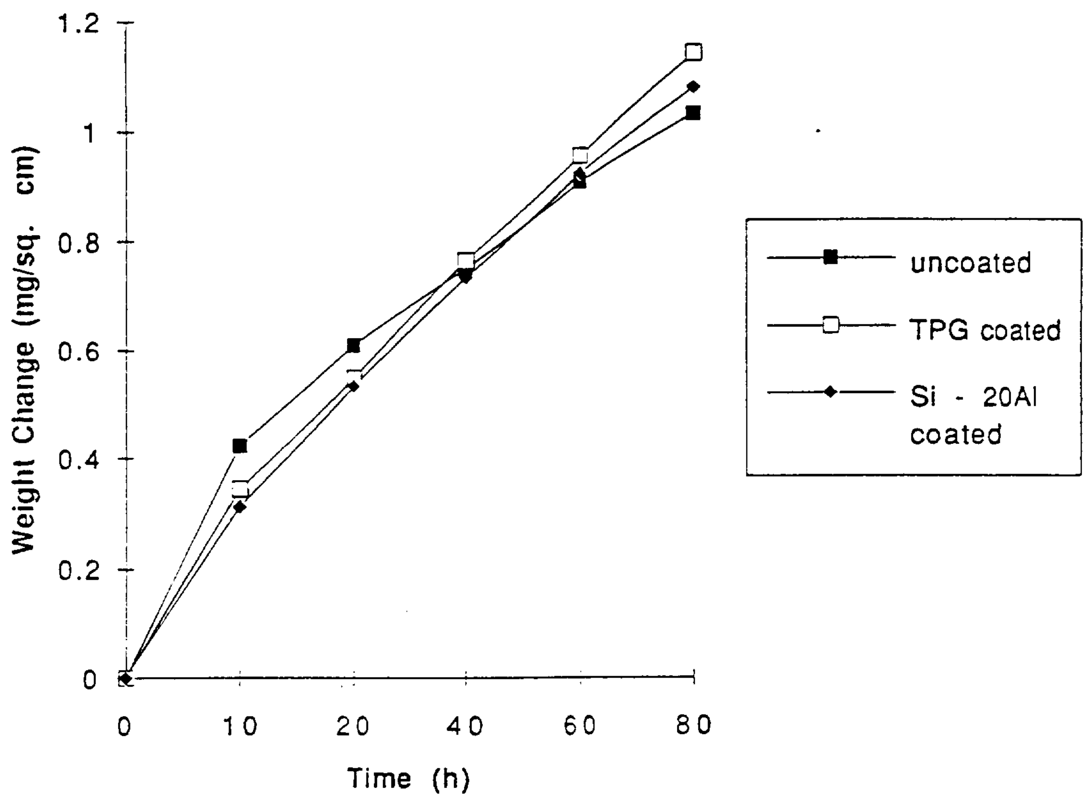

Fig. 7. Weight change vs time data for IN617 discs oxidized in air at 982 deg. C.

No. hrs.	uncoated	TPG coated	Si - 20Al coated	
0	0	0	0	
20	2.0622	2.234	2.1403	
40	2.5933	2.7652	2.6246	
60	2.8745	2.7027	2.8589	
80	3.0933	2.1403	3.062	
100	3.2964	1.3904	3.2651	
120	3.4682	0.0156	3.437	

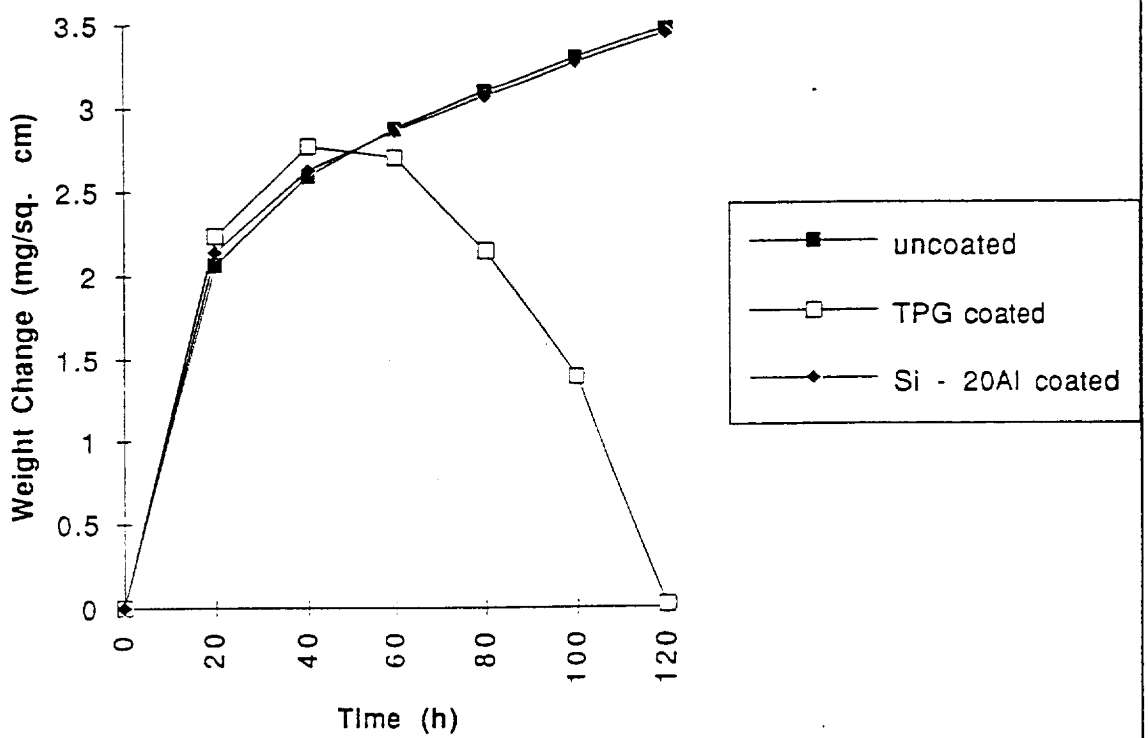

Fig. 8. Weight change vs time data for IN 617 discs oxidized in air at 1100 deg. C.

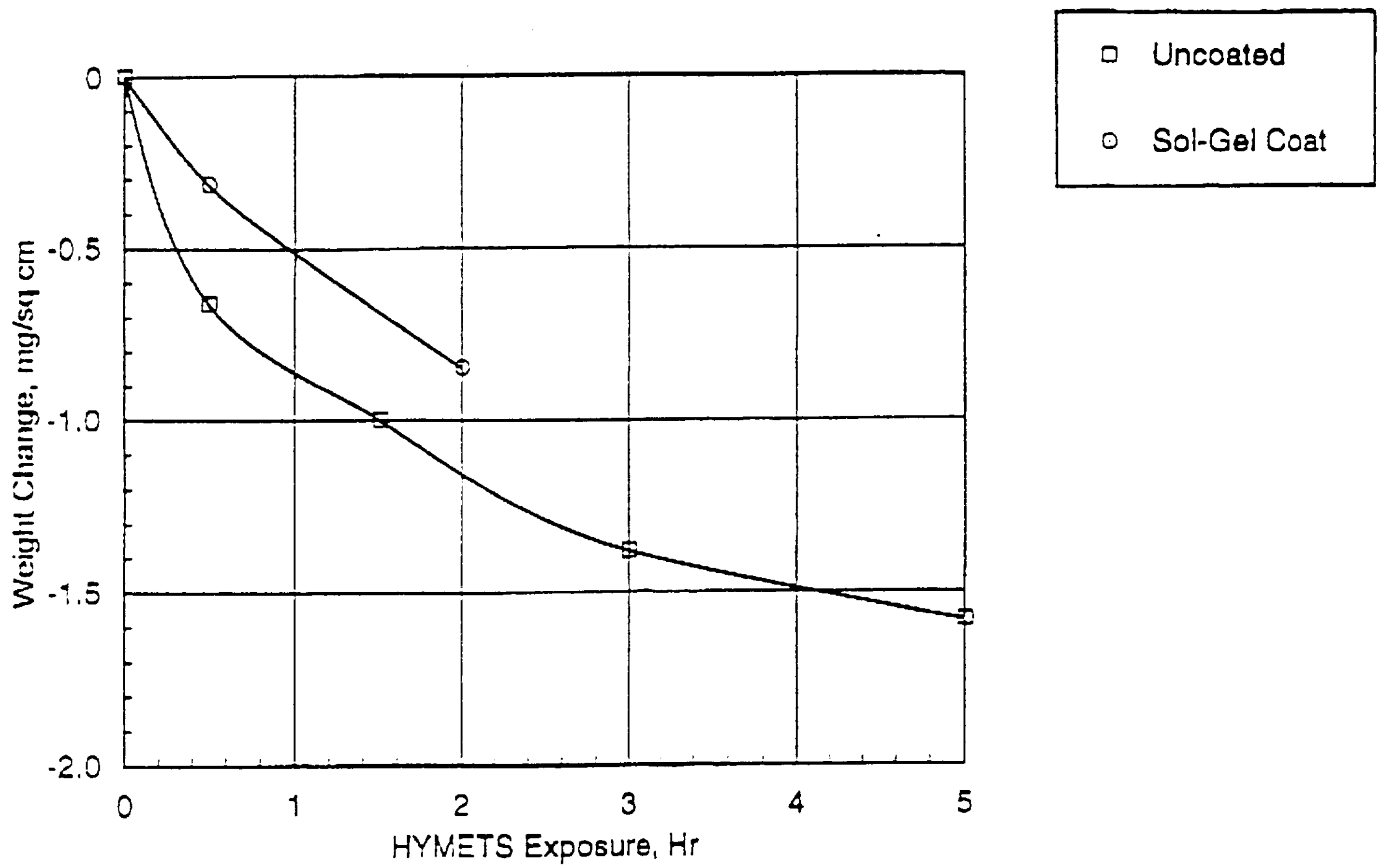

Figure 9. Weight change vs HYMETS exposure at 982°C for uncoated and TPG coated IN 617.

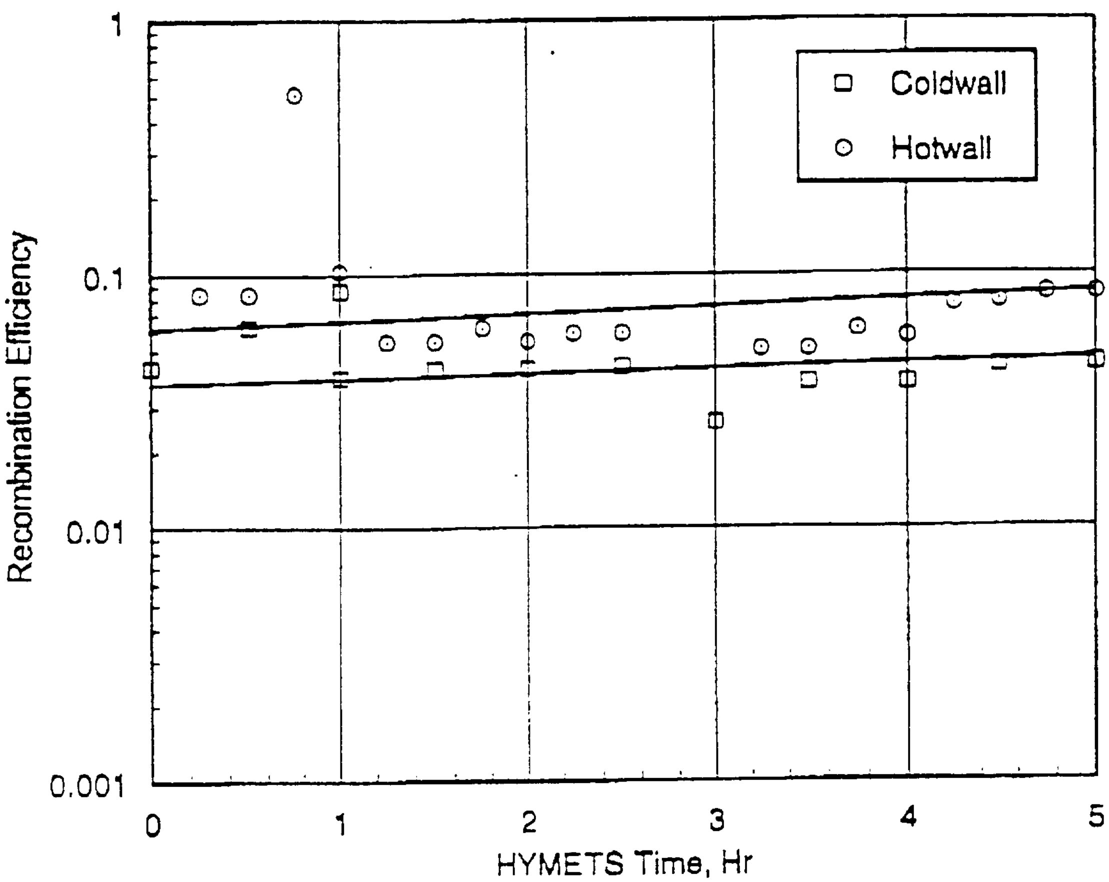

Figure 10. Recombination efficiency vs HYMETS exposure time (982°C) of uncoated IN617.

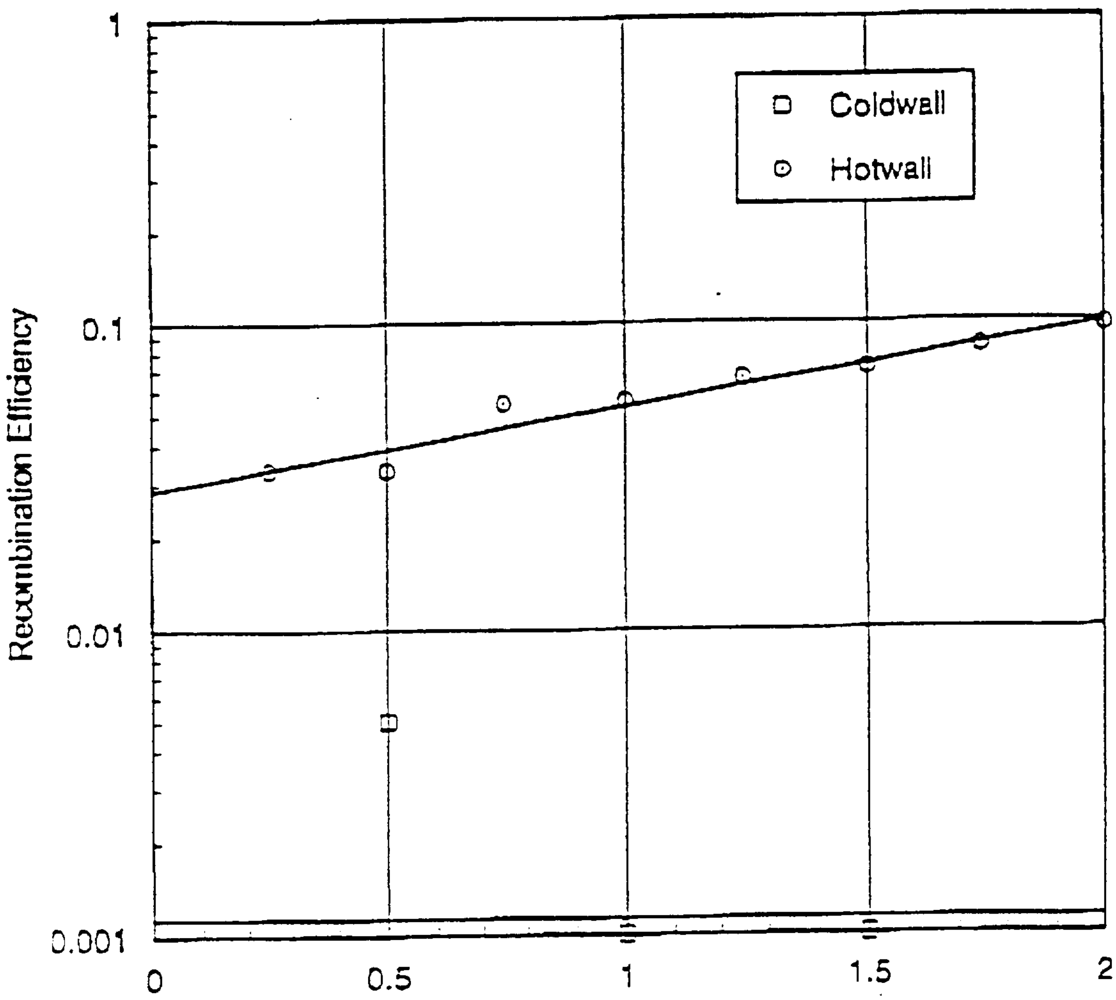

Figure 11. Recombination efficiency vs HYMETS exposure time (982°C) of LaRC sol-gel coated IN617.

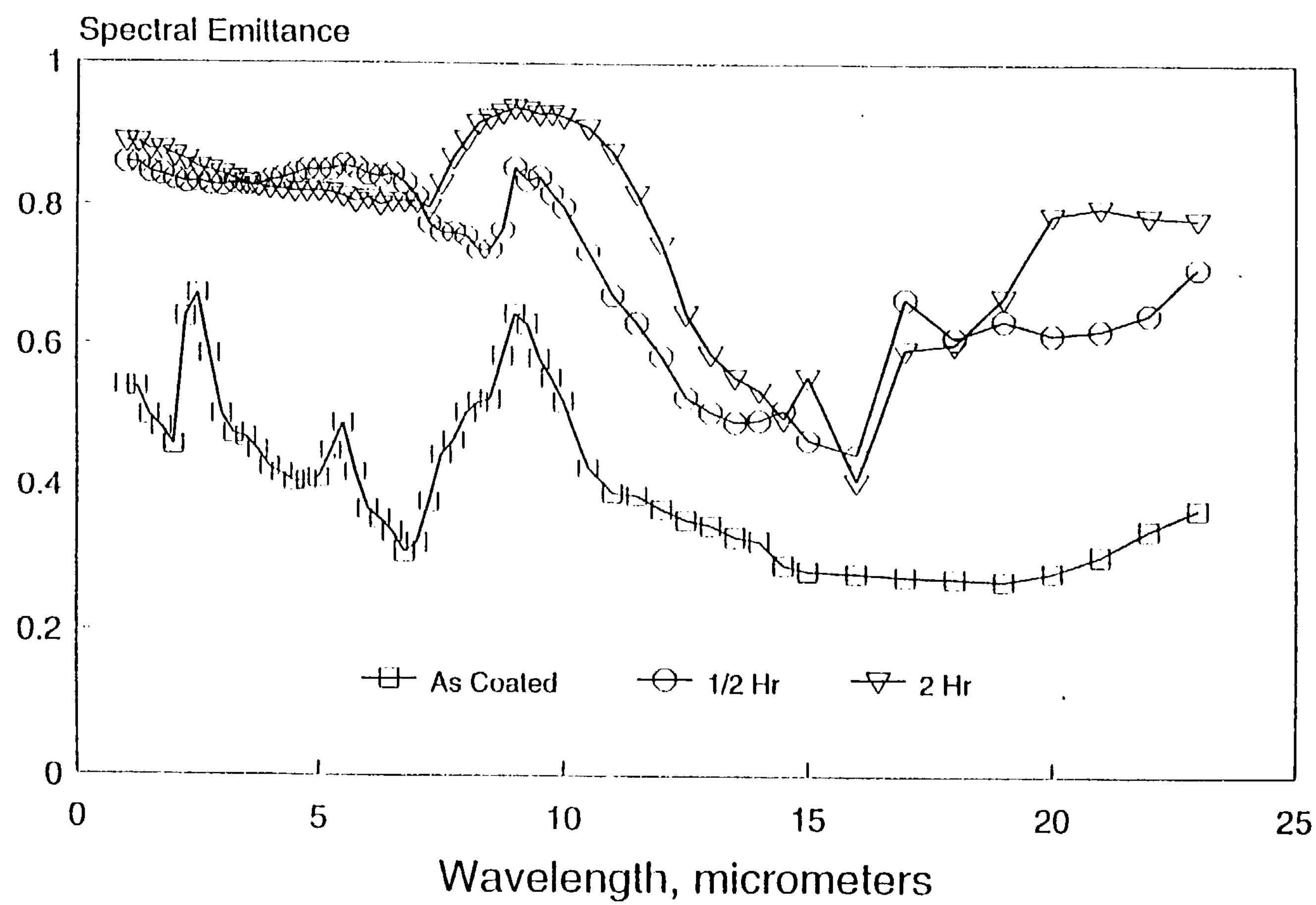

Figure 12. Spectral emittance vs wavelength of TPG coated IN 617 before and after HYMETS exposure at 982°C.

Table V. Total emittance values of as coated and HYMETS exposed samples.

Temperature (°C)	Total Emittance		
	As- coated Condition	After HYMETS Exposure(1/2 h at 982 °C)	After HYMETS Exposure(2 h at 982 °C)
27	0.3926	0.6746	0.7509
327	0.4370	0.7805	0.8138
627	0.4707	0.8131	0.8332
927	0.4916	0.8260	0.8451
982	0.4942	0.8275	0.8467

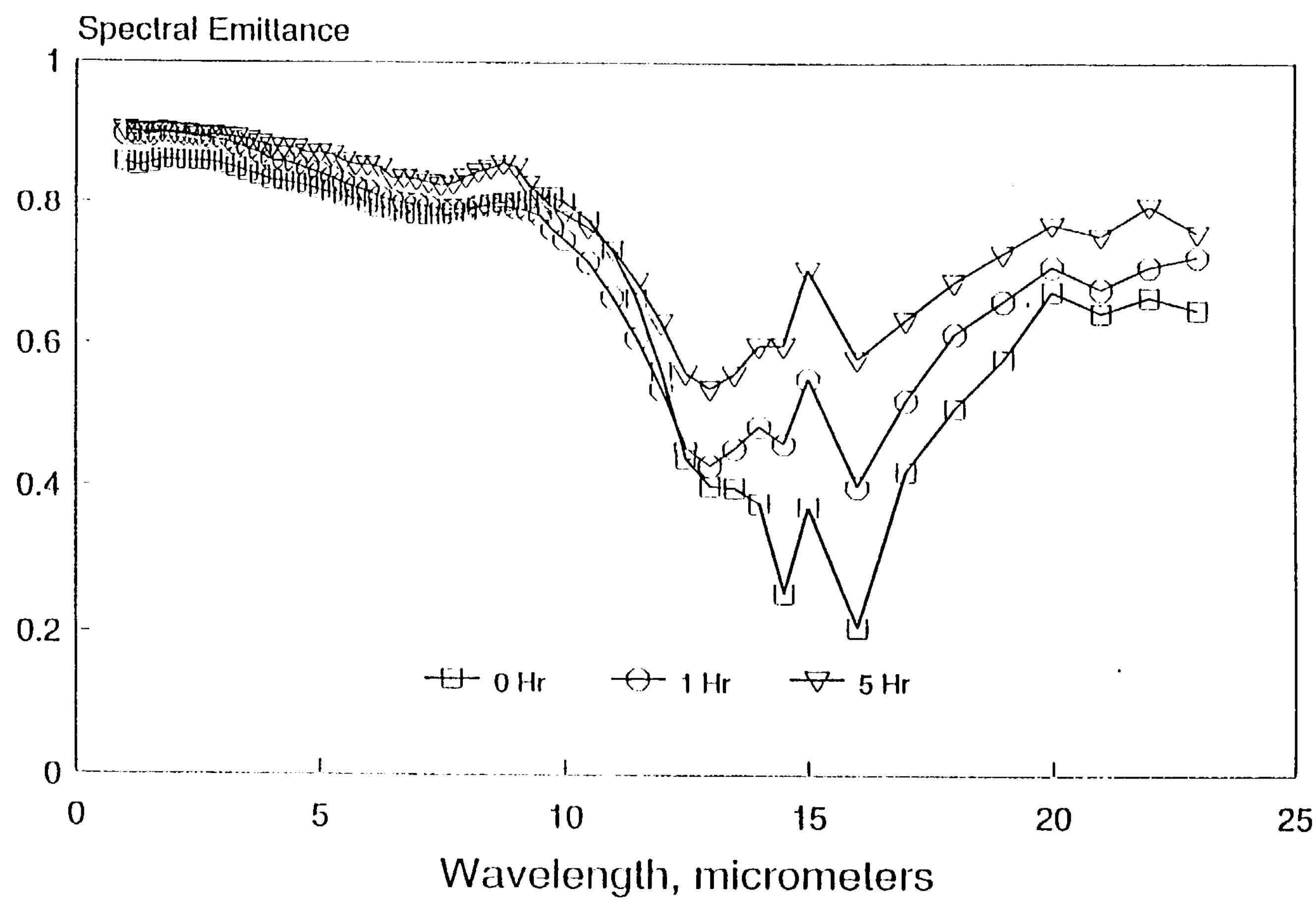

Figure 13. Spectral emittance vs wavelength of IN 617 (bead blast/static oxidation condition) before and after HYMETS exposure at 982°C.

Inorganic Coatings for Waterproofing Ceramic Fibrous Insulation

Replaces Volatile Organic Dimethylethoxysilane (DMES)

- Advantages
  - Non-volatile
  - Permanent
  - No reapplication necessary

- Results To Date
  - Contact angles (θ) > 90^{o} (ZrO_2 and 5%$CaZrO_2$)
  - Reduction in vicinal hydroxyls
  - ~50% Reduction in water absorption (better performance needed)

Coatings for Thermal Control of IN 617

- Objective: DevelopTough, Self-healing Coatings With
  - High emittance
  - Low catalysis
  - High oxidation resistance

- Benefits
  - Lower structural weight
  - Improved structural lifetimes

- Results To Date
  - Improved oxidation resistance (in HYMETS exposure)
  - Total Emittance ~ 0.85 (after HYMETS exposure)
  - Non catalytic coatings effective on IN 617 (low recombination efficiencies)